Atomic Spectroscopy

ISSN: 0195-5373

e-ISSN: 2708-521X

Vol. 41 No. 4

Jul/Aug. 2020

www.at-spectrosc.com

Cover Feature:

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Atomic
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Rapid Analysis of Soil Samples by Laser Ionization Mass Spectrometry

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Received: May 20, 2020; **Revised:** Jun. 05, 2020; **Accepted:** Jun. 05, 2020; **Published:** Aug. 01, 2020.

DOI: 10.46770/AS.2020.04.001

ABSTRACT: In this work, laser ionization mass spectrometry (LIMS) was developed in the laboratory and used to analyze geochemical standard reference soil samples to demonstrate the rapid analytical capability of this technique. With the help of high laser irradiance and low-pressure buffer gas, sufficient atomization and quite uniform ionization can be achieved. Little spectral interference appeared in the spectra produced by LIMS, while the signal intensity is fairly proportional to the element concentration. These features enable LIMS to acquire semi-quantitative analysis without reference materials. To further improve the quantitative accuracy, correction factors can be obtained using reference materials, while these correction factors can virtually be applied for elemental quantitation of all soil samples. The results show that LIMS is a reliable technology for the rapid analysis of metallic and non-metallic elements in soil samples.

INTRODUCTION

Since the time of industrialization, large numbers of harmful substances have been discharged into soil in large quantities, including heavy metals, radioactive elements, organophosphorus pesticides, organochlorine pesticides and so on.¹⁻³ When these harmful substances exceed the self-purification capacity in soil, they will cause changes in the composition, structure and function of soil, thus polluting the environment. Therefore, the detection of elements in soil is necessary to evaluate soil contamination.

Conventionally, geological samples are analyzed by a variety of analytical techniques after cumbersome preparation and decomposition procedures. As the number of samples and elements to be analyzed grows, the complexity of the sample preparation step overshadows that of the actual analytical measurements. Therefore, direct solid analytical techniques are receiving growing interest. So far, the most common mass spectrometric method for the direct analysis of solids mainly includes secondary ion mass spectrometry (SIMS),⁴⁻⁷ laser ionization mass spectrometry (LIMS),⁸⁻¹¹ glow discharge mass spectrometry (GDMS)¹²⁻¹⁴ and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS).¹⁵⁻¹⁸ Compared with

conventional solution-based analytical methods, direct solid analysis by mass spectrometry can provide more efficient analysis without a complicated sample pretreatment.

For LIMS, the ions are generated in the process of laser ablation/ionization and subsequently are pushed into the mass analyzer, then the chemical information of almost all elements on the sample surface can be obtained. Because of the pulse nature of the laser system, the time-of-flight (TOF) mass analyzer is the most suitable among all mass analyzers. However, the ion source of traditional LIMS works under high vacuum, the ions generated by high laser radiance have a large initial energy and wide energy dispersion,^{19, 20} multiply charged ions and polyatomic ions interferences often exist in the spectra,²¹ which affects the spectral resolution and quantitative analysis capability. After addition of the buffer gas to the ion source, the spectral interference from multiply charged ions becomes suppressed by frequent three-body recombination, and polyatomic ions are also reduced by collision dissociation.^{22, 23} The introduction of a buffer gas also effectively solves the broad kinetic energy problem of ions through frequent collisions,²⁴ but at the cost of building a multiple stage vacuum system.

Fig. 1 Schematic diagram of LIMS.

Due to the above merits, the spectra of buffer-gas-assisted LIMS developed in our laboratory results in little interference. Meanwhile, if the signal intensity of the elements is proportional to their concentrations, then the concentration of an element can be obtained by dividing the signal intensity of the element by the total ion current, which directly provides semi-quantitative results of the elements. Consequently, LIMS is capable of direct solids analysis and semi-quantitative analysis of all elements in a solid sample. In this paper, we demonstrate the capability of LIMS for the rapid and semi-quantitative analysis of geochemical standard reference soil samples containing more than 60 elements, some of which differ by nearly seven orders of magnitude.

EXPERIMENTAL

Samples. Powders of geochemical standard reference soil samples (GBW07401, GBW07402, GBW07403, GBW07404, GBW07405, GBW07406, Chinese National Standards Center) were loaded into a die and pressed into a disc using a hydraulic press machine under the pressure of 1×10^7 Pa for 2 min, forming a disc with a diameter of 6 mm and a thickness of 2 mm.

Instrumentation and operating conditions. The schematic diagram of the home-built LIMS is shown in Fig. 1. This system has been described detailed in our previous work.²⁵ A 532 nm Nd:YAG laser (Minilite II, Continuum Inc., USA) with 5 ns pulse duration and 10 Hz operational repetition rate was used as the laser source. The laser beam was focused on the sample surface by an air-spaced doublet lens (ACA254-075-532, Thorlabs Inc., Newton, NJ, USA) to a spot diameter of 50 μm . The pressure of the ion source in the first vacuum stage was generally controlled by an electromagnetic valve. Ultrahigh purity helium (He, 99.999%, Xiamen Linde Gas Ltd., Xiamen, China) was applied as the buffer gas. Double-sided carbon tape was used to mount the samples onto a home-built remote-controlled three-dimensional translation stage.

The ions from the source were transferred through the transmission stage to the TOF mass analyzer. A High-speed ADC

acquisition card (USB9982C, Fcctec Technology Beijing Ltd.) was used to acquire the signal from the microchannel plates. The data were processed using the LIMS data processing program developed by the laboratory, which provides the concentration information of the elements directly. The final spectrum is the sum of $200 \times 250 \mu\text{m}$ (4×5 pixels, 10 shots per pixel). With moving of the sample stage, the time from sample loading to obtaining element information output is approximately 1 min.

RESULTS AND DISCUSSION

For the ion source with buffer gas, the number and type of ions largely depend on the laser irradiance, gas pressure and the distance from sample to skimmer.²⁶ After optimization, the laser irradiance was set at 4.6×10^{10} W/cm², the distance between the laser focusing point and the skimmer was generally controlled at a linear distance of about 14 mm and a helium pressure of 300 Pa.²⁷ The optimized experimental conditions not only reduce the multiply charged ions and polyatomic ions, but also use the majority of ions, so that the elements with low concentration can still be detected.

A typical spectrum of GBW07405 (Fig. 2) was used to demonstrate the analytical capabilities of LIMS for soil samples. The spectrum of GBW07401, GBW07402, GBW07403, GBW07404 and GBW07406 is similar to that of GBW07405. Since soil samples are rich in oxygen, oxide peaks such as ZrO, NbO, LaO and CeO are still observable in the spectrum in Fig. 2, mostly due to the recombination from atomized species. In addition, multicharged ions are generally the most common interference in LIMS spectrum analysis. However, with the introduction of buffer gas, multicharged ion intensities are greatly reduced due to the charge reduction process of three-body recombination, but peaks of doubly charged ions such as Pb^{2+} still occasionally exist. In general, the spectrum of GBW07405 analyzed by LIMS contains little spectral interference, which can be ignored compared with the total ion current.

In this study, we treated standard reference materials as unknown samples to verify the quantitative capabilities of LIMS. The signal intensities cannot precisely represent the concentrations of elements, but when the proportion of interference in the spectrum is low, the concentration of a specific element can be obtained by dividing its peak intensity by the total ion intensity in the spectrum, with each peak multiplied by their corresponding mass weight:

$$w_i = \frac{I_{ij}M_{ij}/R_{ij}}{\sum_k I_k M_k} \quad (1)$$

where w_i represents the mass fraction (element concentration) of element i , I_{ij} represents the peak intensity of isotope j of element i , M_{ij} represents the molar mass of isotope of element i , R_{ij} represents the isotope ratio of isotope j , and $\sum_k I_k M_k$ represents the sum of all peak intensities multiplied by their

Fig. 2 Spectrum of GBW07405 by LIMS. The concentrations of elements are marked on the top of element labels in unit of $\mu\text{g g}^{-1}$.

corresponding mass weights, including all interference peaks. Basically, an isotope with a relatively high isotope ratio and little interference will be chosen for calculating the specific element concentration.

Table 1 shows the comparison between the certified concentrations and measured concentrations of GBW07401, GBW07402 and GBW07403 by LIMS. Besides the elements with high ionization potentials and gas species interference, the measured concentrations for almost all elements are within an order of magnitude of the certified concentrations, which meets the criteria of semi-quantitative analysis. Because laser irradiance of $4.6 \times 10^{10} \text{ W/cm}^2$ would generate a plasma at the temperature of 12000 K,²⁸ sufficient atomization and quite uniform ionization efficiency could be obtained for most elements. In addition, the very small proportion of interference in the spectrum is also an important factor to realize the semi-quantitative result.

To further improve the accuracy of analysis, we divide the measured concentrations in Table 1 by the certified concentrations. Averaged correction factors (f) can be obtained from the result of GBW07401, GBW07402 and GBW07403, as listed in Table 1. Thus Eq. 1 can be converted to:

$$w_i = f_i \cdot \frac{I_{ij}M_{ij}/R_{ij}}{\sum_k I_k M_k} \quad (2)$$

where w_i is the measured concentration after correction. With Eq. 2 established, the corrected concentration of the other three samples, GBW07404, GBW07405 and GBW07406, can be obtained, as listed in Table 2. The correction factor further

reduces the deviation between the measured concentration and the certified concentration, which is within the range of five times. Due to the influence of many factors such as laser power density, ion transmission efficiency, and resolution of the mass analyzer, the ability of this instrument to detect low-concentration elements is somewhat deficient, but it is able to meet the requirements of direct semi-quantitative analysis of soil samples.

CONCLUSIONS

Owing to the introduction of buffer gas in the ion source, the LIMS system proves to be a suitable technology for rapid detection of multiple elements in soil with little or no sample preparation. Geochemical standard reference soils were selected as the samples to verify the semi-quantitative ability of LIMS, where the molar concentration of the element is approximately equal to the signal intensity divided by the total ion current. The results of this study show that LIMS has great semi-quantitative capability, covering 6 orders of magnitude of dynamic detection range. After obtaining the correction factors, the measured concentrations of all elements were closer to their certified values. We believe that in the near future, with the application of more sensitive detectors, multi-channel acquisition and acquisition of equipment with higher resolution (Bits), the dynamic range and quantitative accuracy of LIMS will be further improved. It has been shown that the LIMS technique can greatly facilitate the determination of elements in solids and enabled us to monitor the heavy-metal contamination in soils.

Table 1. Results of Averaged Measured Concentrations for Elements in GBW07401, GBW07402, GBW07403 by LIMS

	Certified conc (µg/g)			Measured conc for LIMS (µg/g)			Average correction factor (f)
	GBW07401	GBW07402	GBW07403	GBW07401	GBW07402	GBW07403	
Ag	0.35	0.054	0.091		3.49	1.83	28.25
As	34	13.7	4.4	121.48	107.12	34.42	6.41
B	50	36	23	6.57	7.61	3.54	0.17
Ba	590	930	1210	3357	10412.22	13589.8	9.37
Be	2.5	1.8	1.4	0.59	0.32	0.35	0.22
Bi	1.2	0.38	0.17				
Br	2.9	4.5	4.3	48.22	96.86	24.25	14.6
Cd	4.3	0.071	0.06				
Ce	70	402	39	365.52	3111.76	165.53	5.74
Cl	70	62	57	568.04	760.08	490.69	9.66
Co	14.2	8.7	5.5	131.46	841.41	68.46	39.47
Cr	62	47	32	846.62	650.04	663.04	16.07
Cs	9	4.9	3.2	109	65.13	32.98	11.9
Cu	21	16.3	11.4	250.38	260.84	213.04	15.54
Dy	4.6	4.4	2.6				
Er	2.6	2.1	1.5				
Eu	1	3	0.72	2.50	12.56		2.23
F	506	2240	246	27.17	136.39	26.39	0.07
Ga	19.3	12	13.7	222.83	265.04	272.46	17.84
Gd	4.6	7.8	2.9				
Ge	1.34	1.2	1.16			47.57	13.67
Hf	6.8	5.8	6.8				
Hg	0.032	0.015	0.06				
Ho	0.87	0.93	0.53				
I	1.8	1.8	1.3	13.85	18.66	13.48	9.48
In	0.08	0.09	0.031	2.29			9.53
La	34	164	21	173.59	992.75	71.76	4.86
Li	35	22	18.4	77.87	38.44	24.12	1.76
Lu	0.41	0.32	0.29	1.6			1.3
Mn	1760	510	304	13445.37	3232.6	1836.67	6.67
Mo	1.4	0.98	0.31				
N	1870	630	640	4866.01	10432.5	8998.59	11.07
Nb	16.6	27	9.3	45.03	86.36	32.72	3.14
Nd	28	210	18.4	76.59	1284.13	12.89	3.18
Ni	20.4	19.4	12	97.53	162.9	98.79	7.14
P	735	446	320	294.45	195.45	157.47	0.44
Pb	98	20	26	886.43	253.83	453.11	13.05
Pr	7.5	57	4.8	38.05	456.64	20.12	5.76
Rb	140	88	85	1257.94	880.17	763.66	9.32
S	310	210	123	393.14	727.82	458.19	1.97
Sb	0.87	1.3	0.44			0.41	0.31
Sc	11.2	10.7	5				
Se	0.14	0.16	0.09			2.34	8.67
Sm	5.2	18	3.3				
Sn	6.1	3	2.5	51.8		19.57	5.44
Sr	155	187	380	540.51	975.52	1707.04	4.4
Ta	1.4	0.78	0.76				
Tb	0.75	0.97	0.49	1.07	2.39		1.29
Te	0.058	0.033	0.039				
Th	11.6	16.6	6	3.61	2.43		0.15
Ti	4830	2710	2240	19030.62	8875.84	8187.99	3.62
Tl	1	0.62	0.48				
Tm	0.42	0.42	0.28				
U	3.3	1.4	1.3				
V	86	62	36	391.85	369.17	226.42	5.6
W	3.1	1.08	0.96				
Y	25	22	15	49.3	59.59	24.8	2.11
Yb	2.7	2	1.7				
Zn	680	42	31	1068.21	198.31	149.6	3.71
Zr	245	219	246	307.02	257.92	138.52	1
Si	292133	342300	348693	245029	348156	398570	1
Al	75071	54582	64800	186382	97089	162228	2.26

Table 1. continued

	Certified conc (µg/g)			Measured conc for LIMS (µg/g)			Average correction factor (f)
	GBW07401	GBW07402	GBW07403	GBW07401	GBW07402	GBW07403	
Fe	46208	29073	17889	266022	171960	109582	5.96
Mg	10860	6240	3480	25923	19886	9954	2.81
Na	12316	12019	20106	25462	35253	48457	2.47
Ca	12286	16857	9071	45738	89659	39146	4.45
K	21491	21077	25226	133803	155598	156426	6.6
C	21100	7500	5500	5235	4212	3588	0.49
O	439835	470951	481334	17127	31777	32806	0.06

Table 2. Results of Averaged Measured Concentrations for Elements after Correcting in GBW07404, GBW07405, GBW07406 by LIMS

	Certified conc (µg/g)			Measured conc for LIMS (µg/g)		
	GBW07404	GBW07405	GBW07406	GBW07404	GBW07405	GBW07406
Ag	0.07	4.4	0.2	0.17	0.58	0.2
As	58	412	220	18.45	202.36	143.99
B	97	53	57	62.72	53.43	63.09
Ba	213	296	118	91.01	124.99	73.98
Be	1.85	2	4.4	0.51	1.58	3.46
Bi	1.04	41	49		51.78	318.29
Br	4	1.5	8	3.5	2.91	5.06
Cd	0.35	0.45	0.13			
Ce	136	91	66	91.22	60.42	61.86
Cl	39	76	95	544.35	560.6	331.32
Co	22	12	7.6	2.91	1.56	1.05
Cr	370	118	75	216.86	42.61	36.1
Cs	21.4	15	10.8	6.72	3.69	4.46
Cu	40	144	390	23.19	34.80	91.63
Dy	6.6	3.7	3.3			
Er	4.5	2.4	2.2			
Eu	0.85	0.82	0.66			
F	540	603	906	774.06	911.43	863.3
Ga	31	32	30	11.06	11.59	14.67
Gd	4.7	3.5	3.4			
Ge	1.9	2.6	3.2			
Hf	14	8.1	7.5			
Hg	0.59	0.29	0.072		16.13	
Ho	1.46	0.77	0.69			
I	9.4	3.8	19.4	4.08	2.77	14.75
In	0.12	4.1	0.84		2.66	0.72
La	53	36	30	35.87	18.61	26.96
Li	55	56	36	22.52	14.77	14.91
Lu	0.75	0.42	0.42			
Mn	1420	1360	1450	1307.75	1112.46	1562.35
Mo	2.6	4.6	18			198.05
N	1000	610	740	964.35	1450.16	826.33
Nb	38	23	27	25.13	18.64	36.76
Nd	27	24	21		15.44	25.32
Ni	64	40	53	32.69	26.28	37.72
P	695	390	303	739.5	566.2	537.51
Pb	58	552	314	20.88	216.66	200
Pr	8.4	7	5.8	1.25	2.88	3.8
Rb	75	117	237	29.95	37.08	92.47
S	180	410	260	192.7	413.27	339.92
Sb	6.3	35	60	13.98	362.62	917.55
Sc	20	17	15.5		0.08	
Se	0.64	1.6	1.34		0.51	0.57
Sm	4.4	4	3.8			
Sn	5.7	18	72		20.43	133.73
Sr	77	42	39	49.24	27.78	36.62
Ta	3.1	1.8	5.3			7.49
Tb	0.94	0.7	0.61			0.62

Table 2. continued

	Certified conc (µg/g)			Measured conc for LIMS (µg/g)		
	GBW07404	GBW07405	GBW07406	GBW07404	GBW07405	GBW07406
Te	0.16	5	0.4		17.81	
Th	27	23	23	115.6	248.5	270.06
Ti	10800	6290	4390	6710.65	3988.09	4350.35
Tl	0.94	1.6	2.4			
Tm	0.7	0.41	0.4			
U	6.7	6.5	6.7		13.74	16
V	247	166	130	158.54	145.27	169.18
W	6.2	34	90	65.09	149.42	566.65
Y	39	21	19	34.73	17.69	21.89
Yb	4.8	2.8	2.7			
Zn	210	494	97	125.89	264.95	71.98
Zr	500	272	220	562.93	353.42	298.6
Si	237767	245327	265673	207800	230458	211805
Al	124147	114247	112394	103334	52231	101636
Fe	75289	90051	61063	70977	86029	71892
Mg	2940	3660	2040	1445	2316	1441
Na	816	890	1410	655	474	709
Ca	1857	714	1571	1405	249	1033
K	8547	12447	14106	5078	5082	5776
C	6500	3500	8300	16598	11084	9257
O	418637	425864	434442	359361	545508	385529

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors gratefully thank the Natural Science Foundation of China (21974116) for financial support of this work.

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